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ALKALI-AGGREGATE REACTION IN CALIFORNIA CONCRETE AGGREGATES

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OUTLINE OF REPORT

	Page
Abstract	3
Introduction	3
Alkali-aggregate reaction	3
Evidence	3
Causes	4
Reactive aggregate constituents	5
Reactive California aggregates	6
Prevention of reaction	10
References	10

Illustrations

Figure		Page
1.	Graph showing expansion of mortar bars	4
2.	Photo of cracks in Parker Dam	4
3.	Photo of cracks in pier	5
4.	Photo of popout around shale fragment	5
5.	Photo of repaired section of bridge railing	6
6.	Photo of pattern cracking in bridge pier	6
7.	Photo of popout around shale fragment	7
8.	Photo of cracking in bridge pier	7
9.	Photo of pattern cracking in concrete floor	8
10.	Photo of cracking in steps	8
11.	Graph showing expansion plotted against percent reactive aggregate	8
12.	Map of California showing distribution of reactive rocks	9

ABSTRACT

The principal cement-aggregate reactions occurring in California are between cement alkali and opaline shale or intermediate to acid volcanic rocks. Expansion, cracking and deterioration usually result from such reactions. The reactivity of an aggregate can be estimated by service history, mortar bars, chemical tests, and petrographic examination. Reaction may be inhibited by limiting the cement alkalies or by adding a corrective pozzolan.

INTRODUCTION

For more than a decade certain California concrete aggregates have been known to be chemically reactive with high alkali cements. Consequently a great deal of research has been done on these aggregates to determine the exact nature of the reaction and to establish which specific rock types enter into the reaction. Studies have been made to determine methods of preventing reaction and tests have been devised for estimating the susceptibility of an aggregate. Much of the resulting data is unpublished and that which has been published is disseminated through the literature. The purpose of this report is to bring this information together rather than to present new material or concepts.

The principal cement-aggregate reaction is termed alkali-aggregate reaction. It is a chemical process in which soluble alkalies (chiefly sodium and potassium) released by the hydration of high alkali cement react with siliceous constituents of the aggregate to produce alkali silica gel. Expansion and deterioration of the concrete normally accompanies the process. Although the nature of deterioration depends in part upon the type of structure, it is generally characterized by cracking, and in extreme cases by displacement of cracked blocks, and may necessitate expensive repairs or even complete replacement. Although alkali-aggregate reaction may not in itself be so serious, it

may facilitate breakdown by other processes such as freezing and thawing or wetting and drying.

As minerals and rocks make up the bulk of the aggregates involved, the subject of alkali-aggregate reaction is of interest to geologists, particularly petrographers, who are the best fitted to deal with the problems of explaining the phenomenon and of predicting the reactivity of untried aggregates. Petrographic examination is the most rapid method of preliminary evaluation of aggregates.

Numerous organizations have taken part in the investigation of alkali-aggregate reaction. Some of the first research was done by the California Division of Highways Materials and Research Department in Sacramento under the direction of T. E. Stanton. This laboratory has made numerous tests with a wide variety of aggregate materials from all parts of the State.

The U. S. Bureau of Reclamation is one of the most active agencies investigating in this field. Studies are made in a laboratory maintained by the regional office in Sacramento and by the Engineering Laboratories in Denver. Reports by members of the staff of the Denver laboratories constitute one of the best sources of information on this and related subjects.

In the course of planning and construction of various engineering structures the U. S. Corps of Engineers Pacific Division Testing Laboratory formerly in Sausalito has studied many aggregates in the southwest although very little of their data has been published.

Acknowledgment. The writer is indebted to Dr. Richard C. Mielenz, Head, Petrographic Laboratory, U. S. Bureau of Reclamation, Denver, Colorado, who has kindly read and criticized the manuscript of this paper.

ALKALI-AGGREGATE REACTION

Evidence

Expansion. Expansion of concrete, one of the most common manifestations of alkali-aggregate reaction, varies in rate and quantity under varying conditions and materials. It is an approximately quantitative measure of reactivity, although anomalies are common. Unlike some of the minor surface phenomena associated with reactivity, expansion affects the entire mass of concrete. The results depend upon the type of structure; commonly cracks develop by volume changes, forcing such engineering structures as gates or generators out of alignment, and buckling paving or curbing.

Laboratory experiments with mortar bars have produced expansion in excess of 1 percent in 1 year. Experiments have shown that expansion is dependent upon high alkali cement, reactive aggregate and available moisture. Figure 1 illustrates such experimental results.

Popouts. Popouts are surface features formed by localized expansion which spalls off irregular- to conical-shaped fragments an inch to several inches across. They usually develop in concrete containing aggregate having a small percentage of reactive material in the coarse fraction. Such large reaction particles act as centers of reaction and expansion.

Pattern Cracking and Microfractures. The largest and most prominent fractures originate as the result of stresses

* University of Southern California, Los Angeles. Manuscript submitted for publication May 1952.

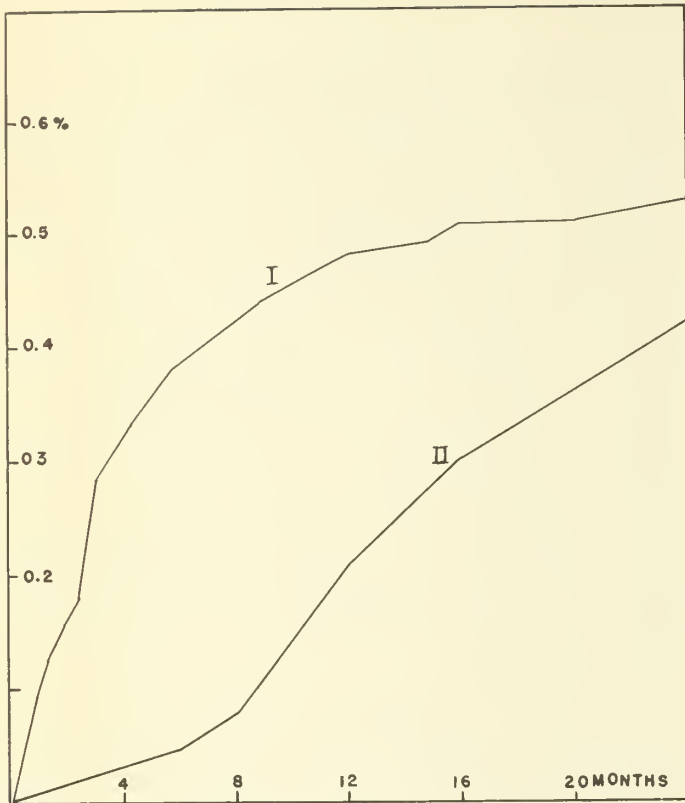


FIGURE 1. Graph showing expansion of mortar bars using high alkali cement and reactive California aggregates. Curve I—Friant andesite (from McConnell et al. 1950); Curve II—Saticoy aggregate (opaline shale) (from Stanton 1942).

arising from expansion, but others, shown in some structures as a network of cracks, have a more obscure origin. The size of fractures and complexity of pattern varies widely; in the more seriously affected structures the openings thus produced may be filled with secondary products of decomposition.

Cracks of similar appearance may be produced by over finishing or excessive water but such cracks are generally limited to the surface.

Cracking of concrete always results in lowered strength; however, a weakening may occur without such obvious features as visible cracks. Stresses developed in the concrete may be insufficient to cause rupture but enough to accelerate breakdown under such mechanical distortion as compression.

Mortar bar tests have shown that expansion due to alkali-aggregate reaction is accompanied by a decline in strength and dynamic modulus of elasticity. In some tests tensile strength decreased more rapidly than compressive strength.

Siliceous Gels. Siliceous gels also are good evidence of reaction between cement and aggregate. The gel, which forms on surfaces or in voids within the concrete, ranges in consistency from watery and gelatinous to rubbery. Desiccation or carbonation occurs upon exposure to the atmosphere, when the gel becomes hard and white. Chemical analyses show that the gels consist chiefly of silica (50 to 80 percent), alkalis (5 to 26 percent), and water.

Reaction Rims. The chemical reaction between alkalis and rock or mineral fragment proceeds inward from the surface of the fragment. In certain rock types the affected portion is distinct from the unaffected portion, the former being darker in reflected light and lighter in transmitted light. Such rims are most common in vitreous or hemi-crystalline andesites, dacites and rhyolites. As pointed out by McConnell et al.¹ all rims of this appearance are not due to alkali reaction; they may be formed by weathering or some other geologic agent. Rims can be assumed to be indicative of reactivity only if they are much more common in the concrete than in the unused aggregate. If they occur around rock or mineral fragments known to be reactive their significance is greater.

Causes

Chemistry of the Reactions. The exact nature of the chemical reaction involved is not known but it appears likely that sodium and potassium released during hydration of the cement is concentrated as setting up occurs. They react with unstable siliceous materials such as volcanic glass, opal, etc. to form alkali-silica gel. In at least some cases the reaction may release alkalis of the aggregate which in turn react with unaltered aggregate. Thus reactions may go on indefinitely, as for example at Stewart Mountain Dam, Arizona, where reaction has continued for 20 years.²

¹ McConnell, D., Mielenz, R. C., Holland, W. Y., and Greene, K. T., Petrology of concrete affected by cement-aggregate reaction: Geol. Soc. America Mem. Berkeley volume, pp. 234-235, 1950.

² Mielenz, R. C., personal communication, 1952.

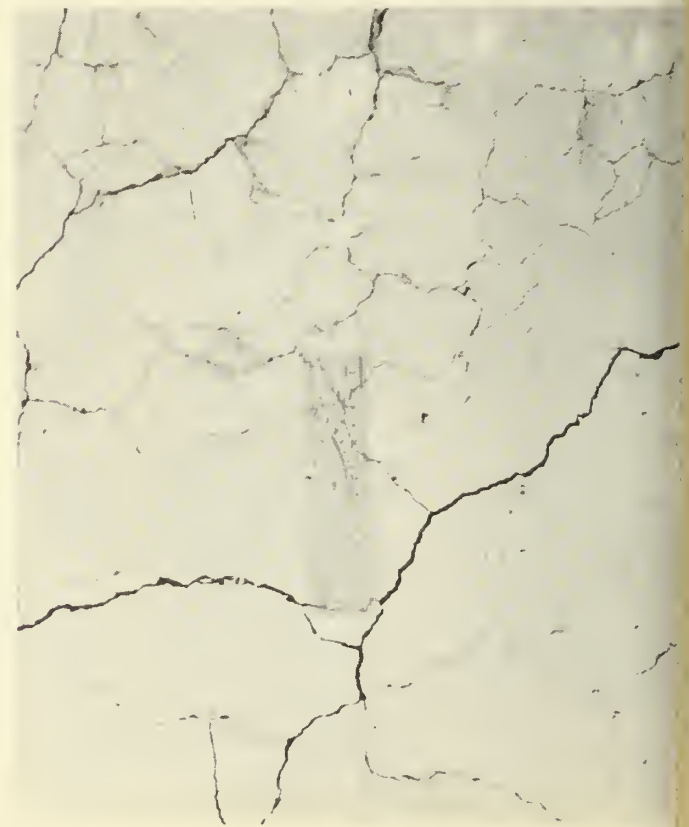


FIGURE 2. Parker Dam. Cracks shown are the result of alkali aggregate reaction.



FIGURE 3. Cracks in pier, Sixth Street Bridge, Los Angeles.

Mechanism of Reaction. Silica gel formed in aggregate particles is surrounded in part by cement paste which acts as a semipermeable membrane. If water is available it is absorbed osmotically by the gel. Osmotic pressures thus developed within the gel may exceed the strength of the enclosing concrete and result in fractures. More gel then accumulates in the fractures which in turn expand by inhibition of water. Pressure in excess of 500 P.S.I. has been produced experimentally.³

Miscellaneous Factors. Some structures built with a given aggregate have been found to deteriorate whereas other structures made of the same aggregate show no signs of deterioration. The difference is believed to be due to differences in the alkali content of the cements. Similar differences have been observed in mortar bar experiments. Other conditions being equal, expansion is roughly equivalent to the alkali content of the cement. Although the total alkali content (calculated as Na_2O) rarely exceeds 1.5 percent, reactions may take place where concentrations are as low as 0.3 percent. In general, however, an amount of 0.6 percent or less is thought to be safe. It is not definitely known whether this permanently inhibits reaction or merely delays it.

One of the first discoveries in experimental work showed that the amount of expansion is not necessarily proportional to the amount of reactive aggregate. For each reactive material there is a certain percentage giving maximum expansion; more or less than this amount will result in less expansion. In general the more reactive minerals and rocks produce maximum expansion with smaller amounts of aggregate and the less reactive materials require greater amounts for maximum effect. Figure 11 shows these relationships for some California aggregate minerals.

A seemingly anomalous relationship exists between expansion and size of aggregate particles. Very reactive



FIGURE 4. Popout around opaline shale fragment, Sixth Street Bridge, Los Angeles. Scale shown is 6 inches in length.

materials such as opal show increased expansion with decrease in particle size. Very reactive materials such as opal show increased expansion with decrease in particle size, whereas less reactive materials usually show more expansion with larger sizes.

Climatic conditions may be responsible for continuing or accentuating a deterioration initiated by alkali-aggregate reaction. The expansion and cracking, although possibly incipient and imperceptible, renders a concrete more susceptible to such common weathering processes as hydration, solution, carbonation, and freezing and thawing. A slightly reactive aggregate may thus be satisfactory if used in a mild climate but unsatisfactory if used in a rigorous climate. Therefore in the testing and evaluation of aggregate the anticipated conditions of use should be considered before final recommendations are made.

REACTIVE AGGREGATE CONSTITUENTS

Knowledge of the reactivity of a wide variety of materials has become available through practical experience and laboratory tests. Mielenz⁴ has tabulated the rocks and minerals known to be deleterious with high alkali cement. Most common rock-forming minerals react to a very slight, insignificant extent. McConnell et al.⁵ have found the following minerals to be essentially innocuous: quartz, microcline, albite, oligoclase, andesine, bytownite, nepheline, hornblende, diopside, augite, olivine, biotite, phlogopite, muscovite, vermiculite, prochlorite, almandite, kaolin, montmorillonite, serpentine, talc, analcite, stilbite, prehnite, epidote, dolomite, calcite, apatite, and colophane.

⁴ Mielenz, R. C., Petrographic examination of concrete aggregates: Geol. Soc. America Bull., vol. 57, p. 312, 1946.

⁵ McConnell, et al., op. cit., p. 238.

³ McConnell, et al., op. cit., p. 246.

Table 1. *Reactive rocks and minerals (from Mielenz).*

Reactive minerals	Chemical composition	Physical character
Opal	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$	Amorphous
Chalcedony	SiO_2	Cryptocrystalline
Tridymite	SiO_2	fibrous Crystalline
Reactive rocks		Reactive component
Siliceous rocks:		
Opaline chert		Opal
Chalcedonic chert		Chalcedony
Siliceous limestone		Chalcedony and/or opal
Volcanic rocks:*		
Rhyolites and rhyolite tuff		} Volcanic glass, devitrified glass and tridymite
Dacite and dacite tuff		
Andesites and andesite tuff		
Metamorphic rocks:		
Phyllites		Hydromica (?)
Miscellaneous rocks:		
Any rocks containing veinlets, inclusions or grains of the reactive rocks or minerals listed above.		

* The volcanic types listed are known to be reactive; basalts are known to be innocuous; data regarding trachytes, latites and phonolites are lacking.

Reactive California Aggregates

The following discussion does not attempt to include all kinds of alkali-aggregate reaction in California since many data of this type are not published. However, examples of most of the deleterious rocks and minerals are given (see table 1).

Opaline Shales and Related Rocks. Sedimentary rocks of this type are widespread in the Miocene of California.



FIGURE 5. Repaired section of railing, Sixth Street Bridge, Los Angeles.



FIGURE 6. Pattern cracking in pier, Sixth Street Bridge, Los Angeles.

Their lithology has been well described by Bramlette.⁶ All rocks of this group are distinguished by a much higher SiO_2 content than characteristic of the average shale or mudstone. Many types of siliceous rocks occur in the group, there being a complete gradation between the various members. Some of the principal types are: relatively soft, diatomaceous rocks; harder, flinty or porcelaneous rocks; and cherts or cherty shales.

The diatomaceous group consists of diatomaceous shale, diatomaceous mudstone and siltstone, and diatomite. The reactive constituent is believed to be opal composing the diatoms; it has a fairly uniform composition of about 89 percent SiO_2 and 11 percent H_2O (index of refraction 1.440).

Many silica-cemented rocks which are less vitreous than chert have a dull luster similar to unglazed porcelain and show little or no lamination. These are termed porcelainite, and consist chiefly of clay or silt with a large amount of opaline silica.

The term chert is used for dense, vitreous rocks made up largely of opaline silica with some chalcedony. It may show thin banding but there is no tendency to separate along the bands except in the more impure varieties to which the term cherty shale is applied.

Limestone is rare in this group of rocks but impure calcareous or dolomitic rocks form thin beds. These rocks usually contain a small but variable amount of opaline silica and are highly reactive.

This formation is widely distributed. In most areas it has been mapped as the Monterey formation but several other names have been applied locally. The following tabular summary of names of siliceous shale formations in California suggests the wide variation of names used for units at least partly equivalent to the Monterey formation

⁶ Bramlette, M. N., The Monterey formation of California and the origin of its siliceous rocks: U. S. Geol. Survey, Prof. Paper 212, 1946.

Miocene Opaline Shale and Related Rocks.

Locality	Name
Berkeley Hills	Tice shale, Claremont shale
San Pablo Bay	Rodeo shale
Monterey County	Monterey
San Luis Obispo	Monterey
Santa Barbara County	Monterey
McKittrick	Monterey
Modelo Canyon	Modelo
Santa Monica Mts.	Modelo
Puente Hills	Puente
Palos Verdes Hills	Valmonte diatomite, Altamira shale
Dana Point	Monterey
Kettleman Hills	McLure shale
Maricopa	Maricopa

These are the most widespread reactive rocks of the state, consequently they are responsible for damage to many concrete structures by alkali-aggregate reactions and accompanying expansion. Extensive sections of highway in San Luis Obispo and Monterey Counties have required repair or replacement because deleterious aggregate was used.

In Los Angeles, the Sixth Street bridge crossing the Los Angeles River shows considerable damage. Portions of the Sepulveda Dam near Los Angeles are marked by a severe popout condition. The deterioration of a concrete breakwater at Santa Barbara is due at least in part to reactivity of opaline shale in the aggregate.

Andesite from Friant and Vicinity. Certain andesite pebbles known to be reactive have been found in the gravel of the San Joaquin River near Fresno. Although not known in place, they are presumably debris that come from the Sierra Nevada Tertiary lava to the east. Although according to standard acceptance tests the rock has good physical properties, yet its chemical nature places it in the deleterious class. Both service history and laboratory tests indicate its reactivity.



FIGURE 7. Popout around opaline shale fragment, Sixth Street Bridge, Los Angeles.

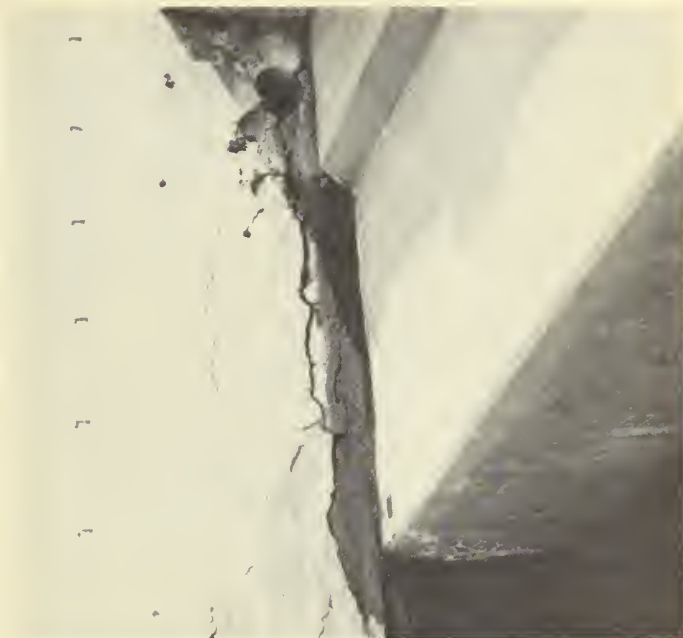


FIGURE 8. Cracking of pier, Sixth Street Bridge, Los Angeles.

Petrographically the rock closely resembles the Parker Dam andesite, one of the first recognized reactive rocks. The average hand specimen is gray to purplish or brown and has small sparse phenocrysts of plagioclase, pyroxene, and hornblende. In thin-section it exhibits massive to distinctly fluidal hyalopilitic texture. Phenocrysts of fresh andesine ranging from 0.1 to 2 millimeters make up 10 percent of the rock. Phenocrysts of hypersthene and hornblende are less abundant. Much of the latter mineral has been replaced by magnetite; and in some sections the hornblende is basaltic. The groundmass comprises 80 to 85 percent of the rock and is composed of small, thin laths of andesine and glass of intermediate composition. Feldspar is generally in excess over glass.

Although information concerning the use of this rock in concrete is limited to aggregate from deposits along the San Joaquin River, nearly identical andesite is known in several areas along the east side of the Central Valley. Concrete in portions of the State Highway in Fresno has been damaged by severe pattern cracking. Certain sections made with low alkali cement show no cracking although the same andesitic aggregate was used.

A few of the first blocks poured in Friant Dam showed minor effects of alkali-aggregate reaction. The later blocks using low alkali cement lack such features although both contain andesitic aggregate.

Parker Dam Aggregate. Portions of Parker Dam, which lies on the southeast border of California exhibit marked effects of reactivity. Expansion of more than 0.1 percent has been measured. Nearby Gene Wash and Copper Basin Dams also show serious distress. The crown of the latter was deflected upstream 5 inches in 9 years owing to expansion. No evidence of reaction has been seen in certain related concrete structures in which low alkali cement was used.

Although the aggregate was obtained from terrace deposits on the Arizona side of the Colorado River, similar deposits and possibly some of the source rocks may be on the California side.



FIGURE 9. Pattern cracking in floor, Law Building, University of Southern California, Los Angeles.

Petrographic studies revealed such reactive rocks as rhyolitic, dacitic, andesitic and trachytic lava and tuff, chalcedonic chert and chalcedonic limestone in the Parker Dam aggregate. Although a considerable variety of volcanic rocks is present, the commonest types are hemi-crystalline, many with hyalopilitic groundmass. In such rocks the vitreous portion has undergone devitrification and the plagioclase microlites show incipient albitization. Ferromagnesian granules make up the remainder of the groundmass. Phenocrysts are oligoclase or andesine and hornblende. The oligoclase may be partially albitized and the andesine and hornblende are frequently bordered by magnetite. Reaction with the cement has produced clarified rims around most of the volcanic particles.

Franciscan Chert. Chert of the Franciscan formation is widespread in the northern and central Coast Ranges, hence it is a prominent constituent in most gravel deposits in these areas. Although such gravel, when used as aggregate, has a satisfactory service history, laboratory tests have shown them to be reactive, probably because of their content of chalcedony and possibly opal. In thin-section the Franciscan chert is seen to consist of varying proportions of granular quartz and fibrous chalcedony. Some specimens are composed largely of an indeterminate, isotropic or nearly isotropic material having a refractive index of about 1.535. Its specific gravity, hardness, and index of refraction indicate that it is probably cryptocrystalline chalcedony rather than opal. A small but variable part of most of the chert is made up of radiolarian remains. In thin-section, areas showing an outline of these organisms are seen to be generally clear and composed of granular quartz. Disseminated fine ferruginous material is abundant in red phases of the chert.

Anorthosite from the Western San Gabriel Mountains. Loughlin⁷ has described the disintegration of cast stone



FIGURE 10. Cracking in steps, Law Building, University of Southern California, Los Angeles.

and stucco using an aggregate of altered anorthosite from the western San Gabriel Mountains. It has been suggested that this disintegration may be due to the reactivity of the zeolite laumontite, one of the alteration products of the andesine in anorthosite. However, laumontite is not known to expand in mortar bars using high alkali cement. Possibly deterioration resulted in part from base exchange processes involving the zeolite. A mixture of 5 parts altered anorthosite and one part calcium carbonate was proven "innocuous" in tests performed by Irving Sherman for K. V. Vail.⁸

⁸ Written communication from K. V. Vail to California Division of Mines, June 12, 1950.

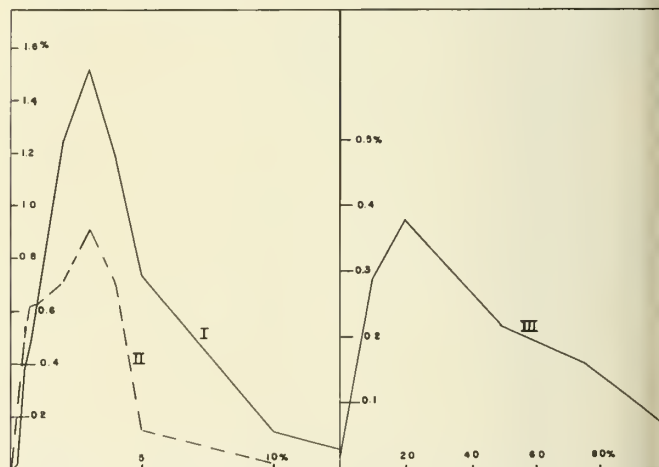


FIGURE 11. Graph showing percent expansion (vertical) plotted against percentage of reactive aggregate replacing inert aggregate. Curve I—opal from Roseville, cement alkali 1.14 percent, age 8 months (from Stanton, 1942); Curve II—opaline chert, Monterey County, cement alkali 1.14 percent, age 8 months (from Stanton 1942); Curve III—Friant andesite, high alkali cement, age 6 months (from McConnell et al. 1950); Curve IV—opal with low alkali cement, (from McConnell et al. 1950).

⁷ Loughlin, G. F., An interesting case of a dangerous aggregate: American Concrete Inst. Proc., vol. 19, p. 142, 1923.

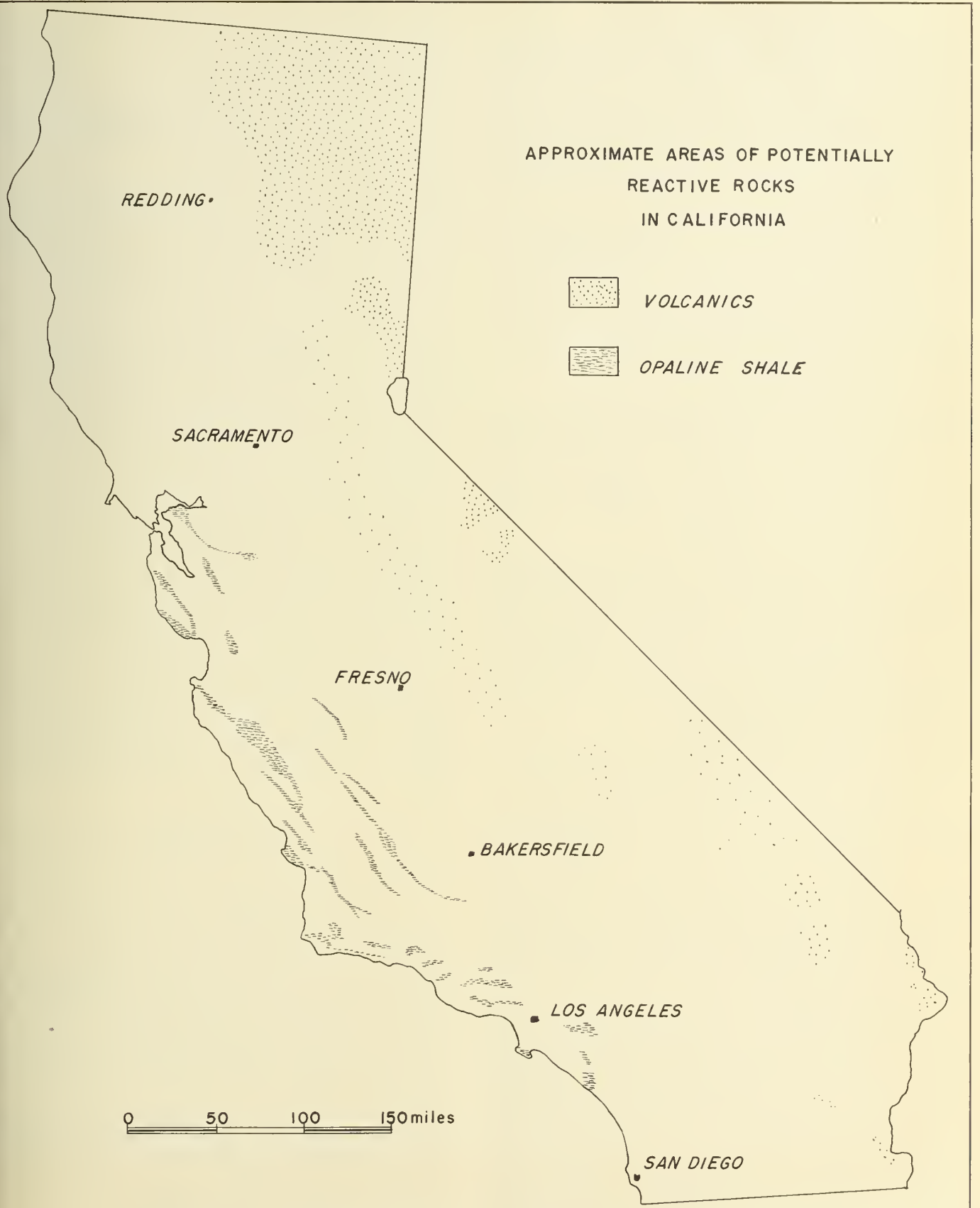


FIGURE 12. Map of California showing approximate distribution of potentially reactive rocks.

PREVENTION OF REACTION

Testing of Material. As there are still some unknown and unpredictable factors it might be argued that the only indisputable, conclusive test is that of actual use. However, information on the service history is available for relatively few aggregates; an aggregate must have been in use for several years as reaction is not always apparent during the first few years. Furthermore, the exact conditions of mixing, placing, and most important, the alkali content of the cement, are rarely known.

The making of mortar bars constitutes one of the most informative laboratory tests. In this process cements of known composition are mixed with various proportions of aggregate and cast in 1- x 1- x 10-inch (or larger) bars. The bars are cured under conditions of controlled temperature and humidity. Their lengths are measured periodically for one or two years at least. Thus the slowness is a great objection to this test, as is the requirement of rather extensive laboratory facilities.

A test which was devised to determine reactivity of aggregate in a short time was described by Mielenz et al.⁹ In brief, the material to be tested is digested in sodium hydroxide and filtered. The filtrate is analyzed for dissolved silica and titrated against a standard acid. The amount of silica and the reduction in alkalinity are a measure of the reactivity. This test, too, requires considerable laboratory work and equipment.

As knowledge of the reactivity of minerals and rocks increases it is becoming possible to evaluate an aggregate by the more rapid method of petrographic study. Although the bulk of the petrographic classifications of constituents of a natural aggregate can be made with a hand lens, the most important determinations require a petrographic microscope. Examples are the distinction of crystalline, hemicrystalline, and glassy groundmasses; of basalt and andesite; quartz, chalcedony and opal.

Chemical Control. Where the use of reactive aggregate is unavoidable, two procedures have been used to reduce or prevent deterioration by cement-aggregate reaction.

The simplest method is that of limiting the alkali content of the cement. As previously stated expansion is generally not serious if the total cement alkalies do not exceed 0.6 percent.

The second preventive method consists of adding a corrective. Many, but not all, pozzolans are correctives. Pozzolans are defined by Mielenz et al.¹⁰ as "natural or artificial siliceous and aluminous substances which are not cementitious themselves but which react with lime in the presence of water at atmospheric temperatures to produce cementitious compounds."

Pozzolans when used as a partial replacement of the portland cement aid in reducing reaction simply by reducing the amount of cement and its contained alkalies. However, to be a satisfactory corrective, a pozzolan must react chemically with or absorb alkalies released by hydrating cement. The alkalies are thus made unavailable for reaction with the aggregate. The cement-pozzolan re-

action presumably takes place mostly before the concrete becomes rigid and, although alkali silica gel may form, it is so disseminated, because of the fine size of the particles, that osmotic pressures do not accumulate. Although there are certain advantages in addition to the corrective action of such pozzolans, some disadvantages may develop. They are: increase in water requirement, decrease in compressive strength, decrease in freezing and thawing durability, and increased drying shrinkage.

The following pozzolans adequately control alkali-aggregate reaction: certain opals and rocks high in opaline silica; some siliceous volcanic glasses; kaolinite (calcined to 1000-1600°F); some diatomaceous earth; certain artificial glasses; and montmorillonite-type clays such as beidellite (calcined to 1000 to 1600°F) in which calcium is the exchangeable cation.

In California the principal pozzolans capable of controlling cement-aggregate reaction are opaline shales and porcelanities of the Monterey or equivalent Miocene formations. They are composed of varying proportion of opal and montmorillonite-type clay with insignificant quantities of quartz, calcite, feldspar and other common minerals. The quality of this material is considerably improved by calcining to 1400°F. Structures in which this pozzolan has been used are: Davis Dam, San Jacinto Tunnel, Golden Gate and San Francisco Bay Bridges, Big Creek Dam No. 7, and some sections of highway paving.

In addition to opaline shales, numerous other natural pozzolans have been used in California. However, none are completely satisfactory correctives; in fact some aid rather than suppress reaction. They include pumicite from Friant used in the Friant Dam, and Pardee Dam; altered rhyolite tuff from the Rosamond formation used in the Los Angeles aqueduct; and argillaceous silt from San Francisco Bay used in Bonneville Dam.

Mortar bars in which a mixture of altered anorthosite and calcite was substituted for high alkali cement gave the following results in one year: 15 percent substitution, expansion reduced 30 percent of expansion of control bar; 25 percent, 57 percent reduction; 40 percent, 72 percent reduction.¹¹

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